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20. Abstract
Attempts to determine the initial vibrational and rotational energy distributions in deuterium fluoride produced from the reaction

$$D + F_2 \rightarrow DF + F$$

are described. The results are compared with those obtained from the measured relaxation method and with data recently produced by other workers.

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EXPERIMENTAL DETERMINATION OF INITIAL VIBRATIONAL AND ROTATIONAL ENERGY DISTRIBUTIONS FROM THE REACTION OF ATOMIC DEUTERIUM WITH MOLECULAR FLUORINE.

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Prepared for

EXPERIMENTAL DETERMINATION OF INITIAL VIBRATIONAL AND ROTATIONAL ENERGY DISTRIBUTIONS FROM THE REACTION OF ATOMIC DEUTERIUM WITH MOLECULAR FLUORINE

As mentioned in a previous report (AFOSR-79-0067) a great deal of effort has been put in by various groups, using both experimental and theoretical techniques, in attempts to understand the dynamics of the simple atom-molecule reactions. In particular the reactions 1, 2 and 4 have been very extensively studied and broad general agreement has been attained between different groups of workers. Reaction 3 has, however, proved to be much more problematical.

$$H + F_2 \cdot HF + F \qquad (1)$$

$$F + H_2 \to HF + H \qquad (2)$$

$$D + F_2 \cdot DF + F \qquad (3)$$

$$F + D_2 \cdot DF + D \qquad (4)$$
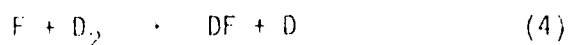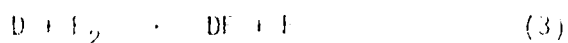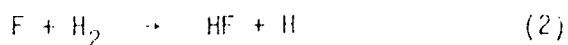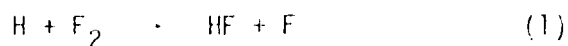
At the time when this work was initiated the only study of the initial vibrational energy distribution in deuterium fluoride was one we had made using the measured relaxation infrared chemiluminescence method (1). Although not completely unambiguous, that study strongly suggested that the most populated vibrational level of deuterium fluoride was $v' = 10$. It also determined relative primary rate constants for formation of deuterium fluoride in vibrational levels $v' = 2$ to $v' = 12$. The results indicated that 62 per cent of the available energy initially entered vibration.

There has often been some conflict between experimental results obtained by the measured relaxation infrared chemiluminescence method and those obtained by the lower pressure arrested relaxation method. This was one of the reasons that a study by the latter method was proposed. Additionally, the measured relaxation method gives no indication of the initial rotational energy

distribution, which is a valuable additional quality so far as chemical laser applications are concerned.

Experimental

The apparatus used for arrested relaxation studies is shown in Figure 1. The design of the reaction cell is critically important. In view of the desirability of operating at the minimum possible pressure it must possess an efficient light collecting system, contain an effective mean of arresting the product state relaxation processes, and provide optimum pumping conditions. It is in the last respect that the present design differs most significantly from those of other workers. Pumping of the cell is effected by means of an Edwards 24 inch F2404 oil diffusion pump backed by an ISC 3000 Edwards rotary pump. The unthrottled throughput for hydrogen is $10 - 1200 \ dm^3$ at a pressure of 10^{-4} torr. Perhaps most important, the entire bottom area of the reaction cell is exposed to the vacuum pump via a liquid nitrogen cooled chevron baffle. The remaining sides and top of the reaction cell are covered by an "inverted trough" of copper plate cooled by continuous passage of liquid nitrogen through copper coils silver soldered to its outer surface. The light collection system is a standard Welsh cell consisting of four semi-circular gold plated mirrors of 150 mm diameter, radius of curvature 530 mm, independently mounted in pairs and capable of individual adjustment from outside the cell.

In order to attempt to improve the efficiency of trapping of vibrationally excited molecule at the cold walls, considerable time was spent in redesigning these so that an approximately ¼" layer of cooled molecular sieve was attached to the inside of the trough. This was achieved by holding the molecular sieve in place with a high transmission gauze. As before the whole assembly was cooled with liquid nitrogen. The relatively poor conductivity of the molecular sieve necessitated that the layer was kept as thin as possible. The efficiency of the new cryogenic pumping system was investigated using the well-known

reactions of atomic fluorine with methane and ethane. Both these alkanes are difficult to pump cryogenically and it was demonstrated successfully that there was a significant improvement with the new system.

Deuterium (Air Products Ltd. 99.999 per cent), fluorine (B.O.C. Ltd. 98.0 per cent) and argon (B.O.C. Ltd. 99.999 per cent) were used without further purification. Deuterium atoms were produced by a 100 W, 2450 MHz microwave discharge in deuterium. Fluorine atoms were produced by a similar discharge technique using carbon tetrafluoride as the precursor.

Due to the extreme toxicity and corrosive nature of fluorine, a number of modifications to the usual gas inlet and outlet systems were necessitated. The molecular fluorine was introduced to the fluorine glass line through ¼ inch copper pipe. This line had previously been evacuated thoroughly to minimize adsorbed water. The flow rate was controlled by a stainless steel needle valve and measured using a calibrated capillary flow meter filled with a full fluorinated oil. Voltalef 90 grease was used on all glass stopcocks and glass to metal connections were made with teflon tubing. Excess fluorine was discharged into a trap containing a mixture of potassium hydroxide pellets and glass beads. The beads prevented trap blockage due to the formation of a solid crust of potassium fluoride.

The fundamental emission from DF spans a region (3.46 μm to 4.60 μm) in which the sensitivity of a conventional lead sulphide detector is low. It was therefore necessary to record the DF spectra in the first overtone region (1.75 μm to 2.96 μm) which lies near the peak of the detector's response.

The infrared spectrum of DF does not lend itself to simple analysis in the same way as hydrogen fluoride. The larger reduced mass and consequent smaller vibrational and rotational spacings result in many near coincidences of vibration-rotation lines within overlapped bands. Consequently a computer simulation technique is essential in order to analyse the spectra. In order to calculate the vibration-rotation line positions with sufficient accuracy

it was found necessary to use a Dunham expression with 16 coefficients. This expression used the Dunham coefficients for HF (2) corrected for DF by means of the isotope relations (3).

$$\frac{Y_{1J}^{i}}{Y_{1J}} = \frac{\mu}{\mu^{i}} \quad (1 + 2J)/2. \tag{5}$$

The trial vibrational and rotational population distributions $(N^{v'J'})$ input to the simulation program were converted to intensities by

$$I_{vJ}^{v'J'} = \frac{N^{v'J'} hc(\omega_{vJ}^{v'J'})^4 F_{vJ}^{v'J'} S_J A_v^{v'}}{(2J' + 1)(\omega_v^{v'})^3} \tag{6}$$

where $I_{vJ}^{v'J'}$ is the intensity and $\omega_{vJ}^{v'J'}$ is the frequency of transition from a state $(v'J')$ to state (v,J). $A_v^{v'}$ is the Einstein coefficient and $\omega_v^{v'}$ is the frequency of the pure vibrational transition $(v' \rightarrow v)$. S_J is the line strength and $F_{vJ}^{v'J'}$ is the rotation-vibration interaction factor, calculated using the full expression of Herman et al. (4). The Einstein coefficients used were those of Sileo and Cool (5).

As stated above, the emission intensity $(I_{vJ}^{v'J'})$ of any particular vibration-rotation line may be related to the population $(N^{v'J'})$ of that state by expression (6). In previous work an approximate expression was used to calculate the rotational contribution to the transition probability. To improve the accuracy of this study, a program was developed to calculate the contribution using the full expression of reference 4.

Results and Analysis

Analysis of the DF spectra would be further complicated by any non-Boltzmann nature of the rotational distributions to be found within any particular vibrational level. Under the previous grant a considerable effort was put into developing computer programs capable of simulating the experimental

distributions.

Initial experiments were carried out without the cryogenic molecular sieve being installed. Under these conditions it was necessary to use relatively high flow rates of the reactant gases in order to obtain detectable emission. The spectra obtained clearly showed that little rotationally excited HF was formed. Furthermore although the HF was vibrationally excited the degree of excitation was lower than that found by the measured relaxation method. The data were analysed by comparison with computer-simulated spectra and the results are shown on Figure 2. These results are consistent with the idea that the residence time in the reaction chamber was too long. Under such conditions the number of collisions would be sufficient to randomize the rotational energy distribution and also lead to vibrational relaxation through collisional and rotational processes.

The later experiments were all carried out using the cooled molecular sieve liner as an additional pumping aid. Certainly this had appreciable advantages so far as allowing additional throughput of reactants as was demonstrated for poorly pumped gases such as those present in the atomic fluorine/methane reaction. When the $D + F_2$ reaction was repeated under these new conditions it was observed that significantly faster pumping speeds were indeed achieved. The resulting infrared spectra were analysed and the results for the vibrational energy distribution in the product hydrogen fluoride are shown in Figure 2. It can be seen from this Figure that a higher degree of vibrational excitation was achieved. However, the maximum population occurred in the $v' = 9$ vibrational level compared with the measured relaxation result which showed the maximum population to be in $v' = 10$. This is again indicative of partial vibrational relaxation which was borne out by the fact that the computer simulation comparison showed these to be very little rotationally excited product. Many further experiments were carried out using different reactant flowrates and different inlet geometries. However, in all cases, basically the same results were obtained and the conclusion was

reluctantly drawn that even with the additional aid of cryogenic pumping, the residence time of the product hydrogen fluoride within the reaction chamber was such that some rotational decay and collisional relaxation took place.

Recently a study of this reaction by a different experimental method has been published (6). This made use of a so-called chemiluminescence mapping method. Results are presented for both the reaction of atomic fluorine with deuterium and atomic deuterium with molecular fluorine. However, whereas the former results are in satisfactory agreement with previously published data, the latter are drastically at variance and show a maximum population in the $v' = 11$ level of DF as can be seen from Figure 2. Taken in isolation these results would appear to be very much more realistic even though the signal-to-noise ratio in the published spectrum is not good. They would seem to bear out the thesis that the residence time under the normal chemiluminescence method conditions, is too long. However, there are several disturbing aspects which need clarification. No data by the chemiluminescence mapping method have been obtained for the H/F_2 reaction for which there was excellent agreement for the vibrational energy distribution in the product HF by the measured and arrested relaxation techniques, obtained independently in different laboratories (7,8). In the work on the H/F_2 system we and others (7,8) demonstrated that it was possible to produce a modified LEPS potential energy surface which could be used in conjunction with classical trajectory calculations to give a satisfactory reproduction of the experimental vibrational energy distribution. Later work showed that this surface could be used to provide a reasonable approximation to the distribution found in the D/F_2 reaction (1). This is to be expected since any isotope effects would be small. However, it is clear that the surface does not provide a good representation of the distribution found by Jardy et al. (6). One is, therefore, forced to the conclusion that unless one accepts a highly improbable isotope effect, the experimental results achieved by the chemiluminescence mapping method results are not compatible with the accepted

results for H/F_2 obtained by two different methods. Obviously this does not negate the chemiluminescence mapping data and may cast doubts on those for H/F_2 although similar experimental results were obtained in different laboratories. The discrepancy is highlighted by the fact that chemiluminescence mapping suggested that 78 of the available energy was present as vibrationally excited product whereas the results for H/F_2 were approximately 20 less. It would be of great interest to see results on the latter reaction by the chemiluminescence mapping method. Until such work is carried out, many questions must remain unanswered.

Although in this work we failed to observe the initial energy distribution from the D/F_2 reaction, it is possible to predict this by making an approximate energy match with the results from H/F_2 by Polanyi et al. (8). One is therefore making the perhaps unreasonable assumption that the vibrational energy distribution for HF is correct. These results are shown in Figure 3 together with our present results obtained using the zeolite cryogenic pumping system. It may be seen from this Figure that the point made earlier concerning a "Boltzmannized" distribution of rotational energy in the DF corresponding to a temperature somewhat less than 300 K is borne out. In the "energy match" results it is necessary to ignore the peak at low rotational quantum numbers in each spectrum since this is due to partial collisional relaxation. The initial rotation energy distribution for DF peaks in $J' = 8$ for $v' = 11$ and gradually moves to $J' = 12$ for $v' = 7$. Trajectory calculations using the potential energy surface described earlier (1) can be used to make a prediction of the initial rotational energy distribution. These results are presented in Figure 4 where it can be seen that the agreement is good. Similar agreement was found for the H/F_2 case. One should not, however, interpret this as an argument against the chemiluminescence mapping results for the vibrational distribution. It is probable that potential energy surfaces giving a strong vibrational energy population inversion would have the same broad characteristics. However, it is likely

that the initial rotational energy distribution found by Polanyi et al. [4]
is correct for H + I₂ since this distribution would be relatively insensitive
to vibrational radiative decay. Hence although the "energy match" procedure
might well give an incorrect picture of vibrational disposal for product SF
it is probably a reasonable approximation to the initial rotational energy
distribution.

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FIGURE CAPTIONS

Figure 1   Diagram of the reaction chamber

Figure 2   Vibrational distributions for the $D + F_2$ reaction

                   ————————   Measured relaxation experiment (ref 1)

                   — — — — —   Arrested relaxation results (without sieve)

                   —·—·—·—   Arrested relaxation results (with sieve)

                   ·············   Chemiluminescence mapping results (ref 6)

Figure 3   Rotational Distribution for the $D + F_2$ reaction

                   — — — — —   Energy match with $H + F_2$ results (ref 8)

                   ————————   Arrested relaxation results (with sieve)

Figure 4   Trajectory rotational energy distributions for the $D + F_2$ reaction
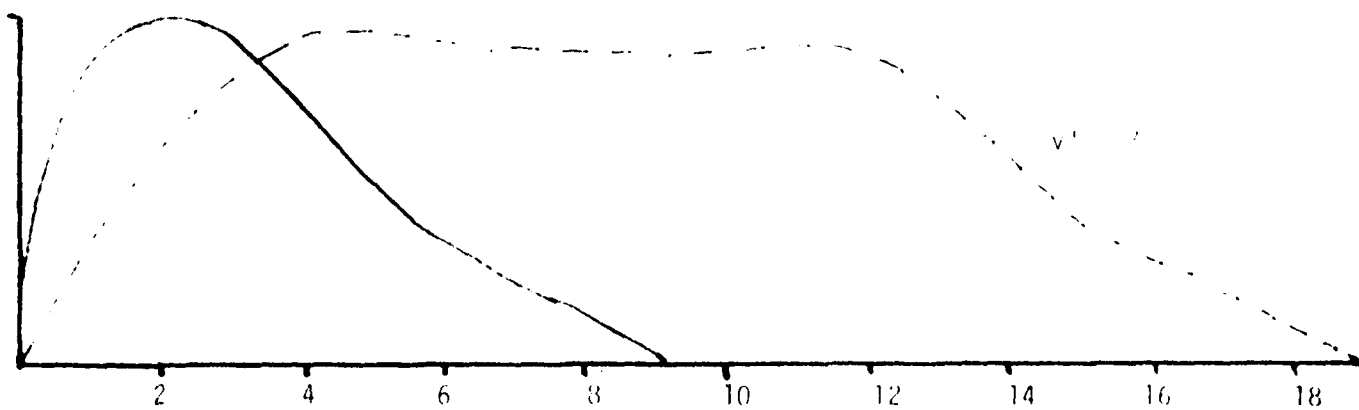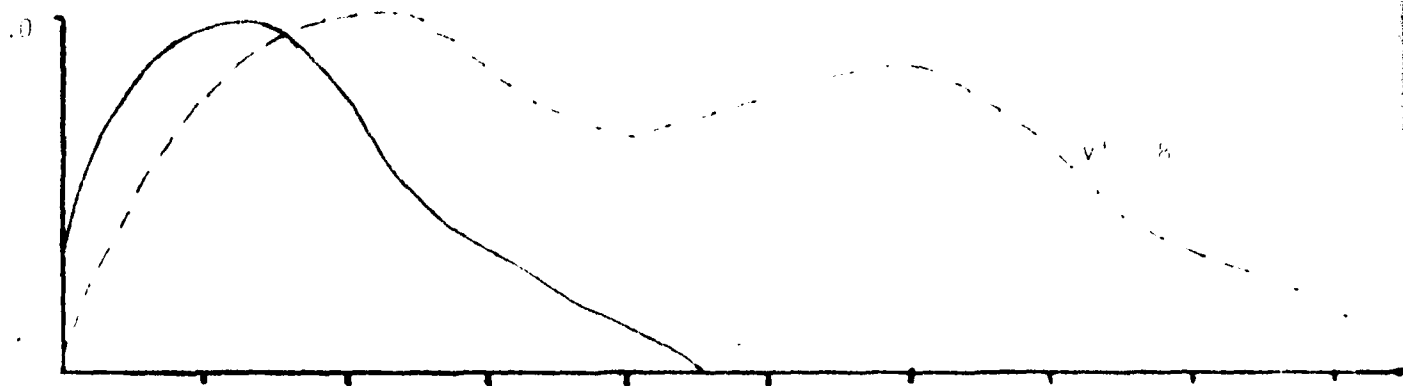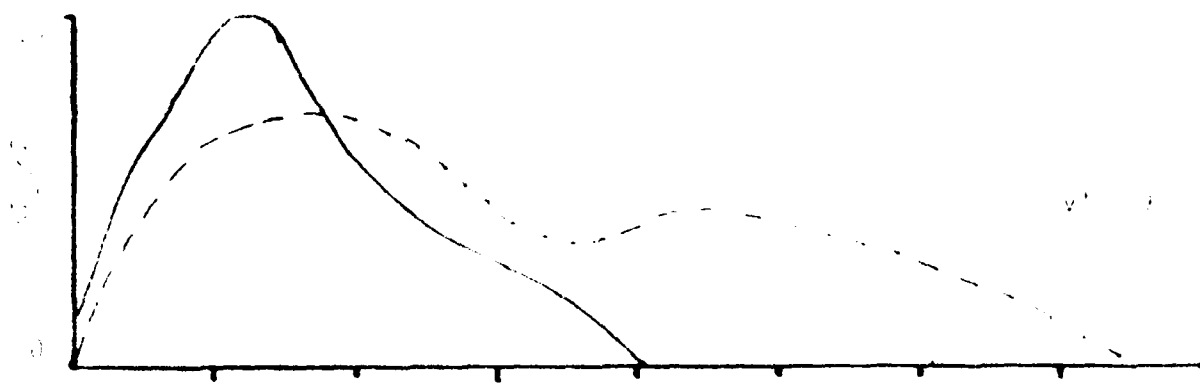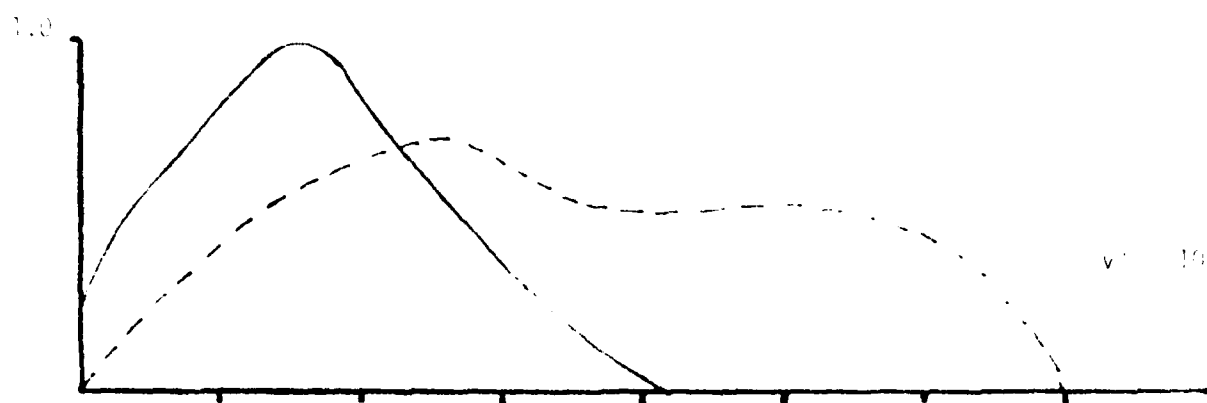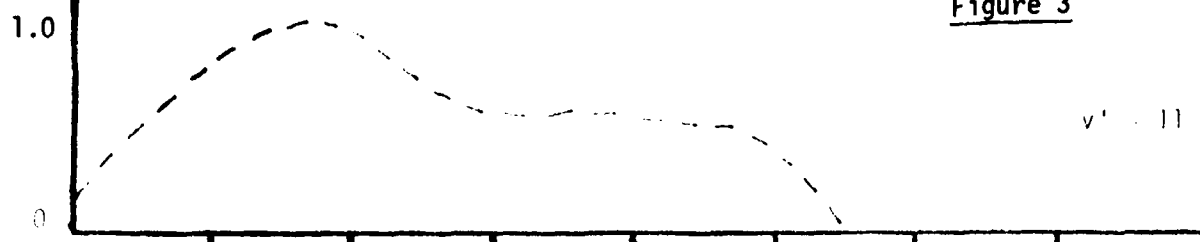
Figure 2
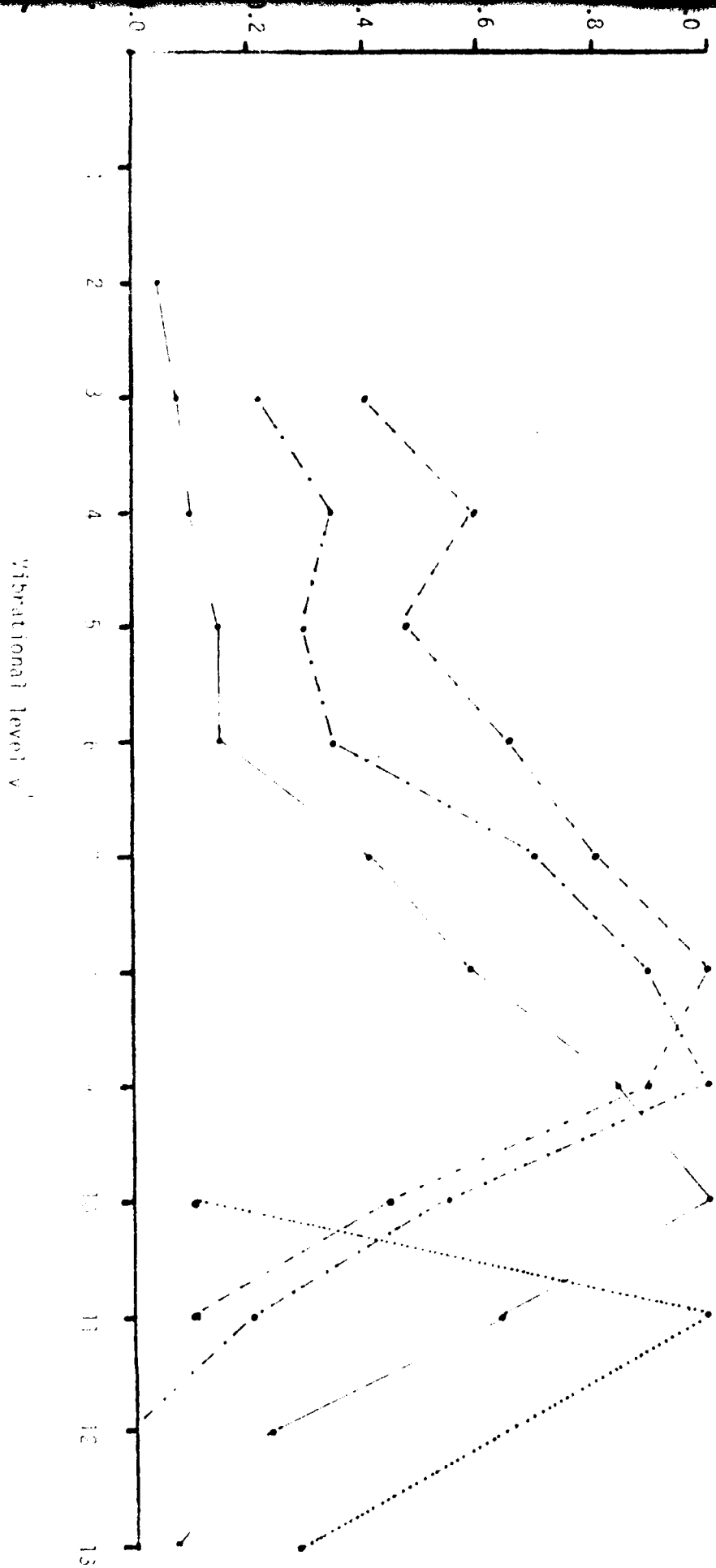
Figure 3

Rotational Quantum Number

Figure 4